Structural, optical and electrical properties of CuO thin films deposited by spray pyrolysis technique: influence annealing process

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In this work, CuO thin films about the synthesis of the thin films are prepared on glass substrate using spray pyrolysis technique at room temperature different annealing times in temperature 450 ^{0}C.In order to study the effect of annealing times onthe structural, optical and electrical properties.XRD analysis has shown that films with a polycrystalline structurehave a(Monoclinic) structure.In addition, the crystallite phase CuO increases with increasing of annealing temperature.Moreover, with a preferred orientation along (002) peak.The optical properties confirmed that the elaborated films have a transmittance of 70%. We have found that the band gap energy (Eg) is a decreasing function with respect to the annealing temperature time. In addition, the electrical resistivity varies from 18.97 to 4.58 KOhm.cm for the films grown at different annealing times.

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1. Introduction

Among metal oxides, copper oxide (CuO) has been an excellent candidate in most technological applications.This material is given special attention in different areas of research and industries because of its appropriate range of applications.In addition, CuO has been the subject of several studies due to its interesting properties as a semiconductor of type p with an optical gap equal to or greater than 2.1 eV [1], simplicity of preparation, abundant in nature, low cost and non-toxic. This material is considered today as one of the most used in photovoltaic module technologies for the manufacture of solar cells [2], because of its high solar absorption, low thermal emission, good electrical properties and high carrier concentration. This material is also promising as an electrode material for the next generation of rechargeable lithium batteries, due to its high theoretical capacity, its safety towards the environment. It is also widely used in gas sensors. As a result, CuO demands are expected to increase rapidly due to its high quality and unique crystal phase. Therefore, this material has been studied to be considered a future material because of its encouraging properties in various other applications, including energy materials [3], supercapacitors [4], magnetic storage [5], photodetectors [6], spintronics [7]and superconductors [8], photocatalysis [9], nanofluids and heat transfer applications, biosensors, and removal of inorganic pollutants [10].Based on these considerations, CuO nanostructures also have more attractive magnetic properties. Luce Vida A Sayson et al also prepared CuO thin films on stainless steel substrates by spraying with a solution and observed the decrease of reduced defects and increase of crystallite size by increasing the annealing temperature and other results. The prepared layers proved the applicability electrode for supercapacitors[a].(Nanostructured CuO thin film deposited on stainless steel using spray pyrolysis as supercapacitor electrode).

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Haifa Ben Saad et al also prepared CuO thin films on glass substrates by spraying with a solution and observed crystallization, reduction of the band gap energy and increase in thickness of the films by increasing the annealing temperature.[b](Investigation on thickness and annealing effects on physical properties and electrical circuit model of CuO sprayed thin films)

The physical properties of copper oxide are strongly related to preparation methods. There is a wide variety of techniques for developing thin CuO films. Examples include cathodic[10], sol gel method [11], laser ablation[12], thermal evaporation [13] and pyrolysis spray[14, 15].The latter was used for the development of our thin films of copper oxide that we subsequently annealed at high temperature.This technique has a definite interest; it is a simple technique and makes it possible to produce materials of a very high purity.

This work represents a study of the structural, optical and electrical properties of thin films of CuO obtained by pyrolysis spray in discontinuous mode and undergoing an annealing of different times in a temperature of 450^0 C.

2. Preparation method

2.1. Experimental details

In this work, we deposited thin films CuO by spray pyrolysis method on cleaned glass substrates. The device used is very simple; it consists of a manual sprayer, in which we put the deposit solution, a sprayer fixed at a distance of 20 cm from the substrate. The nozzle of the sprayer is oriented perpendicular to the substrate, a digital thermometer that displays the temperature of the substrate heated from a thermocouple placed on its surface. To obtain a film of CuO, we sprayed a solution of copper acetate molarity of 0.1 M on substrates of heated glass at 350 ^{0}C for different numbers of sprays from 25 to 150 spray with a step of 25 spray, and after obtaining our films. The latter are annealed for 1.2 and 3 hours at a temperature of 450^0 C.

2.2. Characterization method

The structural, optical and electrical were characterized byPhilipsX'Pert diffractometer with radiation (λ = 1,54 A^0) ,and The Raman signal was recorded using an iHR500 spectrophotometer equipped with charge-coupled device detector. All measurements were carried out at room temperature. The latter scans between 35^0 and 70^0 The optical transmission spectra was recorded with UV-Visible in the wavelength range 400-1000 nm. Electrical resistivity was measured with the four points. The film thickness was measured using a Profilometer, where a diamond stylus crosses the sample from the substrate on the oxide film.

3. Results and discussion

3.1. Structural characterization

The XRD results films are shown in Figure 1. The diffraction peaks show that the prepared films have a polycrystalline nature. According to the (JCPDS N^0 45-0937). The CuO crystalline phases have a monoclinic structure with preferential orientation (002) and (111).With the increase in annealing time, the peaks become more intense and become narrow for the film that was annealedat3 h, revealing the improved crystalline size.

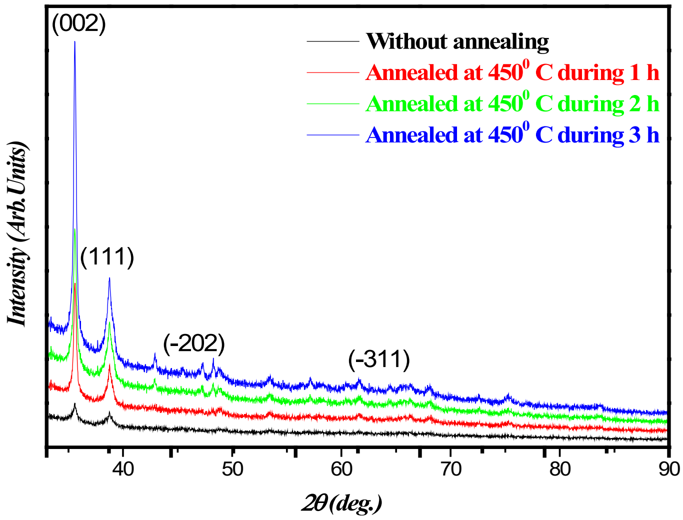

Fig. 1. X-ray diffraction patterns of CuO thin films for different Cu annealing time.

Furthermore, the lattice parameters of CuO thin films have been calculated from the following equations:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 sin^2\beta} - \frac{2hlcos\beta}{a\, c\, sin^2\beta} \quad (1)$$

where a, b, c and β are the lattice parameters for the monoclinic structure, (hkl) are the Miller indices and d is the interplanar distance. The results have been shown in Table 1.The variation of the lattice parameters is remarkably affected by comparing with CuO without annealing. This indicates that annealing has an influence on the crystalline structure. These values are in good agreement with the values reported in the literature [18-21], and the standard JCPDS data card [22].

The variation of the average grain size (D) and the strain ε with annealing of the films were calculated from the peak widths, considering the most intense peak (022), we used the following relationships[23]:

$$D = \frac{0.9.\lambda}{w.cos\theta} \quad (2)$$

$$\varepsilon = \frac{w.cos\theta}{4} \quad (3)$$

where: λ: is the wavelength of the X-ray beam, θ: the diffraction angle, w: the width at half height of the diffraction peak. The variation of the average crystalline and the internal strain for the main peak is shown in Table 1. The size of the grains (or crystallizers), varies between 68 and 88.6 nm when the annealing time varies between 1 and 3 hours. Increased annealing time causes a clear improvement in the structure of copper oxide. When the temperature increases, the atoms will have enough energy to diffuse and occupy normal positions in the site, resulting in an increase in the crystalline and size of the grains that compose the film. The size values of the crystallizers are close to that obtained by Cakmak et al [24].

Table 1. The peak position2θ, FWHM, lattice parameter (a, b and c), crystallite size (D) and strain (ε) of the CuO thin films as a function of annealing time.

Samples	2θ(deg.)	FWHM	a (Å)	b (Å)	c (Å)	D (nm)	ε(%)
CuO without annealing	34,414	0,330	4.48	3.419	5.47	68	0.5
CuO: 450°C 1h	34,431	0,302	4.53	3.42	5.38	70	0.47
CuO: 450°C 2h	34,436	0,301	4.6	3.42	5.23	79.6	0.38
CuO: 450°C 3h	34,425	0,252	4.67	3.42	5.14	88.6	0.23

Figure 2 shows the CuO Raman spectra of our films for different annealing times. The Raman spectra are composed of three main modes Ag and 2Bg located at 278.61 cm^{-1}, 332.39 cm^{-1} and 616.58 cm^{-1}. These peaks are largely reported in the literature [16, 17]. This confirms the presence of a single CuO phase. No other secondary phase modes as Cu_2O peaks are present for all deposited films.

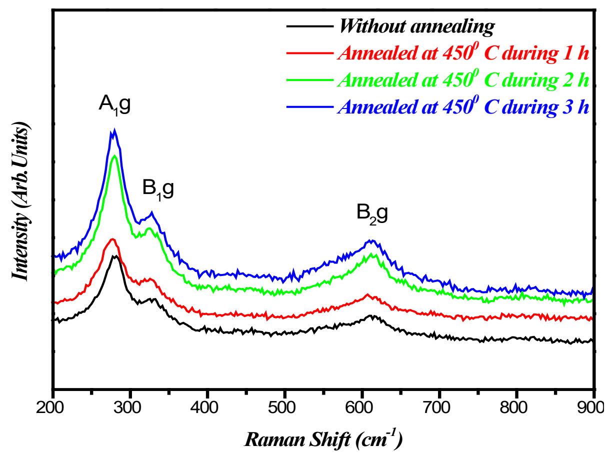

Fig. 2. Raman spectra of the deposited thin films for different annealing time.

3.2. Optical characterization

The evolution of the thickness of the films of CuO as a function of the annealing time is shown in Figure3. It is noted that the thickness of the films increases with the increase of the annealing time, this correlation between the thickness of the films and the annealing time was also obtained by Strýhal et al [25]. These authors performed the thickness measurements using Rutherford Backscatter Spectroscopy.

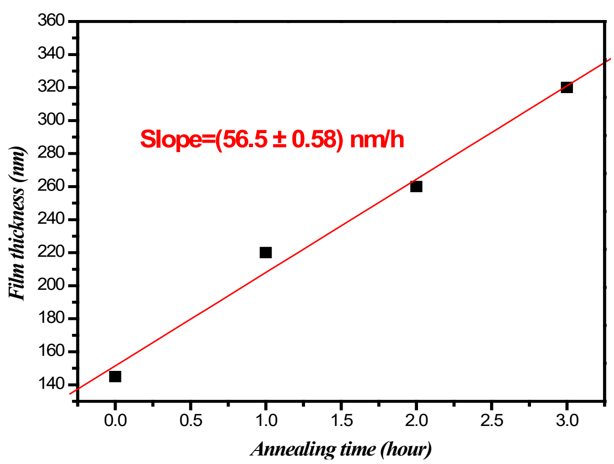

Fig. 3. Variation of the CuO films thickness as a function of the annealing time.

Figure 4 shows the optical transmission spectra of the films obtained by different annealing times. The mean transmission in the visible region varies, depending on the annealing time, between 65 and 15% (Inset of Figure 4), which can be translated by the difference in the structure of these films. As expected from the CuO thin films, the resulting films exhibit a high absorption in the visible region, however, it decreases after 800 nm to the point that the transparency is considerable in the range from 900 nm to 1000 nm. These are the basic characteristics of a good selective solar absorber [26].

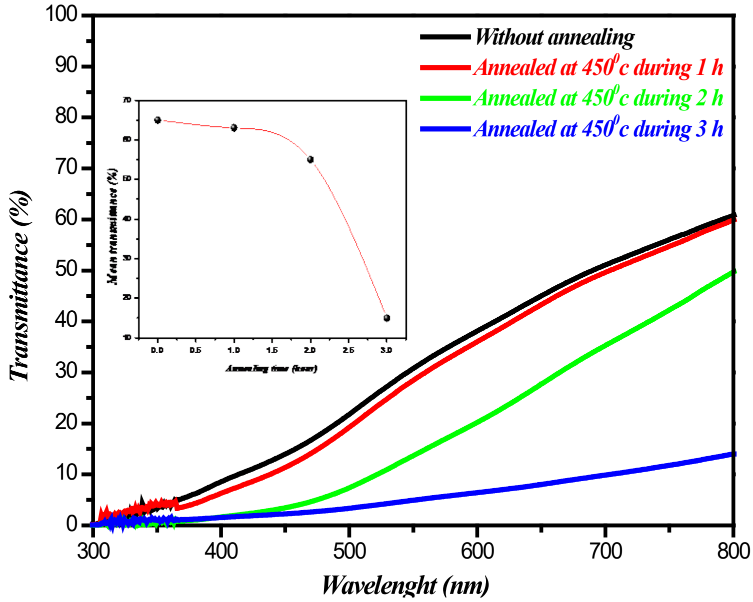

Fig. 4. UV–visible transmittance spectra of the deposited CuO thin films as a function of the annealing time. (Inset: Variation of means transmittance as a function of the annealing time).

The optical energy gap (Eg) andabsorption coefficient is directly related via the Tauc relation [27]:

$$(\alpha h\vartheta)^2 = A\left(h\vartheta - E_g\right) \quad (4)$$

where A constant that characterizes the degree of disorder in an amorphous structure, α: The absorption coefficient, Eg: The optical gap expressed in eV and hv: is the energy of a photonby plotting $(\alpha h\vartheta)^2$against$h\vartheta$, the gap energy can be determined.

The estimated values of the energy band gap (Eg) of without annealing and annealing CuO nanostructures were shown in the (inset of Figure 5). It seems that, among the factors that may possibly modify the band gap, the crystalline size of the CuO films is mainly responsible for the variation of the band gap. The correlation between crystalline size and band gap was shows in Figure 5.

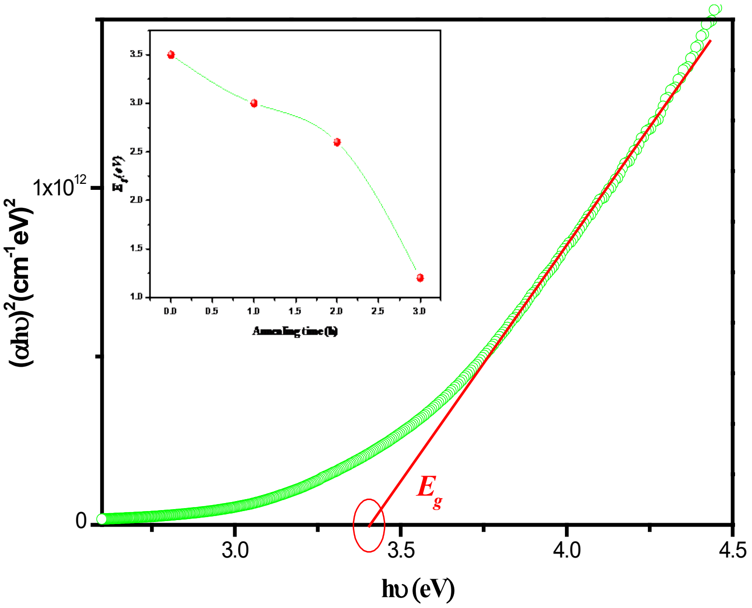

Fig 5. Plot of (αhν)^{2}as a function of the photon energy (hν). (Inset: Variation of the band gap energy Eg as a function of the annealing time).

As a result, we can see the direct correlation between the decreasing band gap energy and the increasing crystallite size. Several works reports the tuning of the band gap energy by the grain size [28-30] where they suppose a direct correlation between these two parameters.

3.3. Electrical characterization

The electrical resistivity of the CuO films, determined after annealing, is presented in Figure 6 as a function of the annealing time.It is found that the resistivity decrease with increasing of annealing temperature. The enhancement in conductivity of CuO thin films is due to improved number of oxygen atoms relative to copper atoms in stoichiometric structure of CuO compound and this effect may convert the type of conductivity in the semiconductor [31].These results match with other references [32-34].

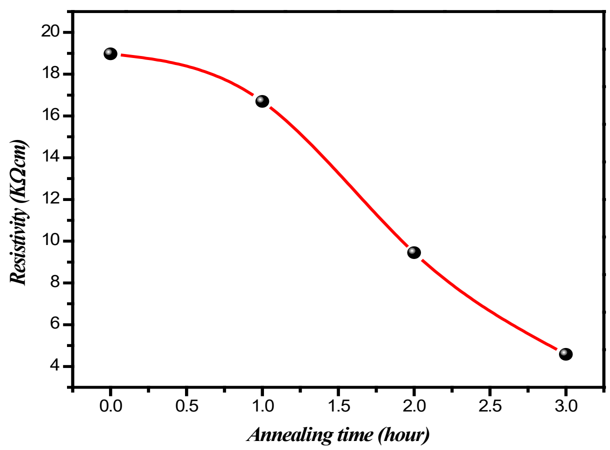

Fig. 6. Variation of the resistivity as a function of annealing time.

4. Conclusion

The work presented focuses on the development and study CuO thin films as a function of annealing time. Annealing is carried out after obtaining the thin films using the pyrolysis spray technique. This technique makes it possible to obtain deposits with properties that vary according to the conditions of elaboration, in order to study the effects of annealing time on properties of the thin films carried out. We have characterized CuO films by different methods: X-ray diffraction for the study of structural properties, UV-Visible spectroscopy for the study of optical properties, and the four-point method for determining the electrical properties of our films. The XRD pattern revealed the presence of the monoclinic polycrystalline CuO. The XRD result was confirmed by Raman spectroscopy. The lattice parameter b remains mainly constant and the crystallite size increased from 68 to 88.6 nm. The increase of the crystallite size was accompanied by a stress relaxation. We noted that the thickness of the CuO films increases with the increase in annealing time. The optical properties of the thin films of CuO are also influenced by annealing, these films are absorbent in UV region and transparent in the visible region, the mean transmittance is of the order of 65 % and a minimum of 15 % for a annealing time of 3 h. The band gap energy varies in the interval [3.5 to 1.2 eV].The electrical characteristics of the thin films of CuO show that the resistivity after annealing decreases to that before annealing. The minimum value obtained always for 3 hours of annealing decreases from 18.97 K Ω.cm to 4.58 KΩ.cm. This result is interpreted by the increase in the number of carriers of charges. Thus, we can say that film annealing is a technique adapted to the development of thin films of CuO of good structural, optical and electrical properties.

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